Abstract

The most common processing of γ-Titaniumaluminides consists of the very expensive double or triple remelting in a vacuum arc furnace (VAR) of afore pressed electrodes of primary materials. By the use of a subsequent spin-casting process so called “master heads” are produced. They are used in investment casting processes where a not inconsiderable amount of the material solidifies in runners and feeders of the casting system or as a skull in the crucible and is obtained as scrap. Due to this high generation of scrap in the production process a suitable recycling process shows great potential to reduce production costs. Based on this circumstance IME Process Metallurgy and Metal Recycling (IME) develops a closed loop recycling process for titanium-aluminide scraps.

The process, which reduces the production costs by more than 35 %, is predicated on a combination of the industrially approved processes vacuum induction melting (VIM), pressure electroslag remelting (PESR) and vacuum arc remelting (VAR). In a first step pretreated γ-TiAl scrap (blasting, etching) is melted in a VIM using specialized ceramic linings and includes pre-deoxidization by calcium addition. The melt is cast into a water cooled copper mould to produce an electrode. In a second step the manufactured electrode is remelted in an inert gas electroslag remelting furnace (IESR) using a continuously activated reactive slag causing a final deoxidization. The third processing step is VAR, in order to remove small slag inclusions as well as dissolved Ca and to allow for hydrogen degassing. Resulting from this process, as a significant innovation for the titanium industry, it is possible to recycle titanium-aluminide scraps and produce material with minimal oxygen content and very small inclusions with a diameter below 5 µm.
Closing the Materials Loop for $\gamma$-TiAl Production

Recycling of Contaminated Scrap

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- Founded Oct. 1870
- Approx. 40,000 students
- 9 faculties, 465 professors
- 118 study courses, 10 in English
- 54% engineering courses
- >12% external students
- 30% female students

No. 1 in Germany for raised funds

No. 1 in Germany for mechanical engineering, metallurgy and metals processing
Our business at IME

- education in non-ferrous metallurgy
  - Bachelor/Master, Diploma and Dr.- degree
- consulting
  - Assessments and studies
- process development
  - Extractive Metallurgy & Recycling
Background: Application Area of TiAl

- **Steady increase in combustion engine requirements:**
  - Lower fuel consumption
  - Reduced pollutant emission
  - Reduced loudness
  - Increased efficiency

- **Substitution of heavy superalloys with high performance \(\gamma\)-TiAl**
  - Low density (3.9 – 4.1 g/cm\(^3\))
  - High melting point (~ 1450 °C)
  - Good oxidation resistance
  - High specific creep resistance

Source: GE Aviation (GEnx)
Background: Conventional $\gamma$-TiAl Production

- VAR Ingot (100 kg)
- Furnace Feed (50 kg)
- Cast Part (10 kg)

Massive scrap → turnings → casting scrap

Up to 90%
IME TiAl Recycling Process

metals/scrap/master alloys → Vacuum Induction Melting → ESR electrodes → Electroslag Remelting → VAR electrodes → Vacuum Arc Remelting → secondary Ti-alloy

- Homogenization
- Deoxidization
- Removal of cavities
- Removal of NMI
- Final deoxidization
- Calcium removal
- Hydrogen removal
Vacuum Induction Melting of TiAl scrap

**Motivation:**
- Consolidation of reclaimed material as well as produced master alloys
- Possibility of a pre-deoxidization
- Production of electrodes for further remelting via PESR

**Challenges:** Contact with ceramic linings
Potential crucible materials for melting titanium

- **CaO**
  - Susceptible to hydration

- **Y$_2$O$_3$**
  - Very expensive

- **CaZrO$_3$**
  - Possible Zr-contamination

- **Y$_2$O$_3$ Coating**
  - Flaking of coating

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Coating
- Flaking of coating
**Selection of crucible material**

**Pre-deoxidization:**
- bulk contaminated TiAl scrap contains >1000 ppm oxygen
- Straight melting in ceramic crucibles end up in oxygen pickups of up to 1000 ppm due to chemical instability

Deoxidization by direct insertion of CaAl$_2$ into the melt

\[
[O]_{\text{TiAl}} + [\text{Ca}]_{\text{TiAl}} = <\text{CaO}>
\]

\[
[O]_{\text{TiAl}} + \{\text{Ca}\} = <\text{CaO}>
\]

< > solid [ ] dissolved { } gaseous

CaO as crucible material is the best choice
Pressure Electroslag Remelting of VIM-cast Electrodes

**Motivation:**
- Remelting using a continuously activated CaF$_2$ slag
  - Reduction of oxygen content
  - Removal of nonmetallic inclusions
- Homogenization of pressed electrodes
- Potential of bulk fluoridization

- pressed electrode with stub
- starting turret
- slag in copper mould
Challenges during PESR of TiAl

- Remelting of different electrode geometries
- Avoidance of concentration gradients
- Removal of nonmetallic inclusions
- Setting a uniform crystal structure
Final Deoxidization of VIM-cast TiAl during PESR

**Motivation:**
- Reduction of oxygen content to ~500 ppm
  - Addition of metallic Ca to provide a continuously activated CaF$_2$ slag

**Challenges:**
- Equilibrium to be maintained during PESR
- Activities of Ca and CaO change
  - Ca is removed by evaporation and through deoxidization
  - CaO activity increases by deoxidization
- Countermeasures to obtain homogeneous ingots
  - CaO dilution by continuous CaF$_2$ addition
  - Ca feed for activity increase and for compensating losses
Potential Bulk Fluoridization to obtain Halogen Effect

- Good oxidation resistance of $\gamma$-TiAl up to 700 – 800 °C
- Higher temperatures result in formation of mixed oxide layer
  - Cracks in the surface
  - Flaking of layers

Source: Zschau (12 h at 900 °C at air)

- High temperature oxidation resistance can be improved by avoiding of mixed oxide layers
  - Micro alloying of halogens
- Only fluorine leads to a sustained increase of oxidation resistance

Source: Zschau (Sample with F implantation)
Vacuum Arc Remelting of deoxidized material

**Motivation:**
- Optional final remelting process
  - Adjustment of crystal structure
  - Removal of potential calcium and hydrogen residues
  - Removal of last nonmetallic inclusions
- Similar to existing standards
Challenges during VAR of secondary TiAl

- Minimization of defects like freckles, white spots, etc.
- Setting a uniform crystal structure
- Adjustment of uniform melting parameters
- Controlled cooling rates to minimize segregations
Summary

**Vacuum Induction Melting:**
- Consolidation of reclaimed material and electrode production
- Possibility of pre-deoxidization

**Pressure Electroslag Remelting:**
- Final deoxidization by continuous Ca addition
- Removal of nonmetallic inclusions
- Possibility of bulk fluoridization

**Vacuum Arc Remelting:**
- Removal of potential Ca and H residues
- Adjustment of crystal structure
Outlook

Balancing of evaporation losses by adjusting VIM melt composition

Possible improvement of oxidation resistance by micro alloying of fluorine

Full validation by large scale series and material characterization
Thank you for your attention!

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